

LOW-SULFUR FUEL BY PRESSURIZED ENTRAINMENT CARBONIZATION OF COAL

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INTRODUCTION

Rapid entrainment carbonization of powdered coal under pressure in a partial hydrogen atmosphere was investigated as a means of producing low-sulfur char for use as a powerplant fuel. Specific objectives of the research were to determine if an acceptable product could be made and to establish the relationship between yields and chemical properties of the char, with special emphasis on type and amount of sulfur compounds in the product. The experiments were conducted with a 4-inch-diameter by 18-inch-high carbonizer according to a composite factorial design (2, 3).¹ Results of the experiments are expressed by empirical mathematical models and are illustrated by the application of response surface analysis.

Previous work with a 4-inch-diameter by 12-inch-high entrainment-type carbonizer showed that chars containing considerably less sulfur than the parent coals could be produced by rapid carbonization (1), and that the most important variables were temperature, pressure, and type of entraining gas. In the experiments with the 18-inch-high carbonizer, all other variables—coal rate, size range and type, residence time, entraining gas rate, and run length—were held constant to determine the effect of the three main factors on char yield and volatile matter concentration and the content of organic, pyritic, and sulfate sulfur in the char.

EQUIPMENT AND PROCEDURE

Carbonization runs were made with the equipment shown in figure 1. The carbonizer was designed for temperatures to 2,000° F, pressures to 500 psi, and coal rates to 500 grams per hour. Coal from a closed pressure-equalized hopper was injected by a vibratory screw feeder into a gas stream that carried the particles at high velocity into the carbonizer. Another stream of gas entered the top of the carbonizer via a preheater that heated the gas to the carbonization temperature.

The carbonizer was 4 inches in diameter by 18 inches long and was made of type 310 alloy steel, schedule 40 pipe. Three pairs of 6-inch-long, semi-circular electrical heating elements enclosed the carbonizing tube. The preheater was a 4-inch-diameter by 2-foot-long coil of ¼-inch stainless steel tubing surrounded by two pairs of 12-inch-long semi-circular electrical heating elements.

All solid and liquid products were recovered from the gas stream. Coarse particles of char were recovered in the lock hopper at the bottom of the carbonizer; char fines and carbon fines were extracted by a hot-dust knockout chamber. Tar and pitch were removed by two knockout chambers in series, and water and light oil were separated by means of a water condenser followed by dry-ice and silica-gel traps. Clean gas was passed through a pressure letdown system, metered, and vented. Yields of dust, tar, light oil, and gas were not determined.

The carbonizer was preheated to the desired (constant) temperature, the system was pressurized to the desired level, and gas flows were set to the predetermined rates and compositions. Coal was then injected to begin the run. The carbonizer was designed to rapidly heat the coal particles as they passed through the 18-inch-long hot zone. Pyrolyzation and devolatilization were effected in less than 1 second. Two hundred grams per hour of 70-percent-through-200-mesh Pittsburgh-bed high-volatile A bituminous coal was processed in 2-hour runs. Entraining gas was admitted at a rate of 20 actual cubic feet per hour. During the run, char was periodically removed from the bottom lock hopper and gas samples were removed for analysis.

¹Underlined numbers in parentheses refer to references at the end of this paper.

EXPERIMENTAL PLAN

Experiments in the carbonization of coal to produce low-sulfur char were carried out and evaluated by means of a 3-step procedure. Carbonization runs were first conducted to obtain data at various combinations of the three major independent variables. These data were then used to develop an empirical mathematical model that described the carbonization system. Finally, response surface analysis was used to interpret the empirical model and predict the relationship between process variables and char yield and quality.

The carbonization runs were carried out according to a composite factorial design covering temperature, pressure, and entraining gas composition—each at five levels. Carbonization temperature was varied from 1,500° to 1,900° F in 100-degree increments and is represented by X_1 . Operating pressure, X_2 , was varied from 0 to 400 psig in 100-psig increments. Entraining gas composition (hydrogen in nitrogen), X_3 , was varied from 0 percent H_2 to 100 percent H_2 at 25 percent intervals. Table 1 shows the levels of the operating conditions.

As illustrated by figure 2, a 3-dimensional coordinate system was assumed with temperature, pressure, and entraining gas composition as the axes. Points at the eight corners of the cube represent the 2-level part of the factorial design; the remaining points represent the composite portion of the design. Each numbered point represents one experimental run and the center represents five additional runs, making a total of 19 runs. Computation of the variance of the system was based on the five runs shown at the center. Actual experimental conditions are shown in the table that accompanies the sketch.

RESULTS

The following results are based on the analyses of data by means of response surface analysis. The 3-dimensional empirical models were developed at the 95-percent confidence level. In other words, 95 percent of the time the results obtained from the empirical model will match the actual data obtained.

As stated, char yield and char quality were of primary interest, the latter being dependent on the concentration of total sulfur, organic sulfur, pyritic sulfur, sulfate sulfur, and volatile matter, and on the heating value and ratio of sulfur content to the heating value. Concentrations of constituents in the char are given as a weight percentage. Table 2 gives the actual experimental data for runs at various combinations of operating conditions.

Char Yield

Figure 3 shows predicted char yield plotted as a function of temperature, pressure, and entraining gas composition. Char yield values of 800, 880, and 960 pounds per ton of coal are shown. Within the limits of the experiments, yields ranged from 646 pounds per ton of coal to 1,222 pounds per ton (table 3). Temperature had a considerable effect on char yield, as was also found in the prior work (1): yields decreased with an increase in temperature. Although pressure variation alone had little effect on char yield, the combined effect of temperature and pressure was important. For example, yields were lower when temperature and pressure were both high or both low. However, when the temperature was the lowest and the pressure was the highest, yields were higher, as was also true when the temperature was the highest and the pressure was the lowest.

Char Quality

Total, Organic, Pyritic, and Sulfate Sulfur

Sulfur does not occur as an element in coal or char; it is present in chemical combination in the form of organic compounds, iron sulfides, and sulfates (4). Total sulfur is the sum of the weight percentage concentrations of all three. As shown in table 3, total sulfur left in the char ranged from 0.7 to 2.5 percent, often a substantial decrease from the amount in the parent coal (2.55 percent). Figure 4 shows total sulfur surfaces for values ranging from 1.0 to 2.5 percent. Crowding of the curved surfaces in the upper left hand corner of the cube clearly shows the decrease in amount of sulfur in the char with increase in the temperature, pressure, and percent hydrogen in the entraining gas. Within the experimental limits, the models indicate that a char can be produced containing a minimum amount of sulfur (0.7 percent) at a temperature of 1,900° F,

pressure of 400 psig, and 91 percent hydrogen in the entraining gas. Production of 0.7 percent sulfur char amounts to more than a 70-percent reduction in sulfur from the original coal.

Organic sulfur accounts for about three-fourths of the total sulfur in the char. A 3-dimensional plot of the values of organic sulfur as a function of temperature, pressure, and entraining gas composition is shown in figure 5. By comparing this figure with the one for total sulfur (figure 4), a similar relationship between the two plots can readily be observed. For instance, as in the case of total sulfur, an increase in temperature, pressure, and percent hydrogen in the entraining gas decreased the amount of organic sulfur in the char. Theoretically, as indicated in table 3, carbonization at 1,900° F, 400 psig, and 100 percent hydrogen in the entraining gas would produce a char containing virtually no organic sulfur.

Approximately one-fourth of the total sulfur in the char is in the form of pyritic sulfur. As shown by figure 6, the amount of pyritic sulfur reached a minimum value of about 0.25 percent at 1,650° F, 230 psig, and 50 percent hydrogen in the entraining gas. Increasing or decreasing values of the variables tends to increase the amount of pyritic sulfur. Pressure and temperature had a greater effect on pyritic sulfur than did percent hydrogen in the entraining gas.

Sulfate sulfur remaining in the chars ranged from 0.01 to 0.06 percent, as indicated in table 2. Since the parent coal contained only 0.06 percent, a change in one or all three variables had no effect on the amount of sulfate sulfur.

Char Sulfur Content Per Unit Heating Value

From a process standpoint, probably the best way to express the amount of sulfur concentration of a fuel is in pounds of sulfur per million Btu heating value of the fuel (char). Ordinarily, this ratio would be a function of the amount of total sulfur in the char and the heating value of the char. However, since the heating value of the char changes very little within the experimental limits (discussed later in this paper), values for the amount of sulfur per heating value are essentially the same as those obtained for percent total sulfur. Figure 7 shows that an increase in temperature, pressure, and percent hydrogen in the entraining gas decreases the amount of sulfur per million Btu. Within the experimental limits, the model indicates that a char containing a minimum of 0.49 pound of sulfur per million Btu could be produced at 1,900° F, 400 psig, and 91 percent hydrogen in the entraining gas.

Volatile Matter and Heating Value

As expected from the results of this experiment and prior work (1), char containing a maximum of volatile matter was produced at relatively low temperatures, and char containing the minimum was produced at higher temperatures. Pressure and type of entraining gas had little effect on the amount of volatile matter remaining in the char. Table 3 indicates that (within the experimental limits) char produced at 1,900° F, 320 psig, and 25 percent hydrogen in the entraining gas would contain the minimum volatile matter—3.8 percent. Char produced at conditions that give the minimum total sulfur content (0.7 percent) would contain 7.38 percent volatile matter. Figure 8 is a graphic portrayal of predicted char volatile matter curves as a function of temperature, pressure, and entraining gas compositions.

As shown in table 2, char heating values ranged between 12,350 and 13,380 Btu/lb. In the 3-dimensional plot (not shown), the portion of the curves that fell within the experimental limits were nearly flat. Because of the narrow range in the data and the flatness of the curves, it can be concluded that neither temperature, pressure, nor percent hydrogen in the entraining gas affected the char heating value.

SUMMARY AND CONCLUSIONS

A low-sulfur char was successfully produced by pressurized carbonization of coal using hydrogen in nitrogen as a hot entraining gas. According to empirical models, a char containing 0.7 percent sulfur, or 0.49 pound sulfur per million Btu, could be produced at 1,900° F, 400 psig, and 91 percent hydrogen in nitrogen. Theoretical characteristics and properties of char produced under these conditions are compared with those of the parent coal in table 4.

Major conclusions drawn from this work are:

- (1) Total sulfur and organic sulfur content of the char and sulfur content per unit of heating value decreased with increase in temperature, pressure, and hydrogen concentration in the entraining gas.
- (2) Pyritic sulfur content depended only on the carbonization temperature and pressure.
- (3) Sulfate sulfur was unaffected by temperature, pressure, or entraining gas composition.
- (4) Carbonization temperature, as would be expected, was of prime importance in regard to the concentration of volatile matter in the resulting char; relatively low temperatures produced a char with a high-volatile matter content, and vice versa.
- (5) Char yield decreased with increase in temperature; pressure and entraining gas composition had no effect. Char heating value was not significantly influenced by any of the three variables.

An empirical approach that included a mathematical model was found to be beneficial in predicting the sulfur content of chars produced from coal over a specified range of operation conditions. The technique was useful for predicting the conditions required for a specified product. For instance, the model for total sulfur indicates that a char containing less than 0.7 percent sulfur could probably be produced at temperatures and pressures higher than those investigated in this experiment.

REFERENCES

1. Belt, R. J., J. S. Wilson, and J. J. S. Sebastian. Continuous Rapid Carbonization of Powdered Coal by Entrainment and Response Surface Analysis of Data. *Fuel*, v. 50, No. 4, October 1971, pp. 381-393.
2. Davies, O. L. Design and Analysis of Industrial Experiments. Editor, Hafner Pub. Co., New York, 1967, 2d ed.
3. Himmelblau, D. M. Process Analysis by Statistical Methods. John Wiley & Sons, Inc., New York, 1968.
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TABLE 1. — Design of the experiment

Factor	Coded design coordinate					Symbol
	-2	-1	0	1	2	
Temperature, °F	1,500	1,600	1,700	1,800	1,900	X ₁
Pressure, psig	0	100	200	300	400	X ₂
Hydrogen in nitrogen, percent	0	25	50	75	100	X ₃

NOTE: Table 2 follows Table 3.

TABLE 3. — Predicted minimum and maximum values for char yield and properties and corresponding process conditions

Char yield and properties	Minimum				Maximum			
	Temp., ° F	Pres., psig	¹ EGC, pct H ₂	Value	Value	Temp ° F	Pres., psig	¹ EGC, pct H ₂
Yield, lb/ton	1,900	400	55	646	1,222	1,500	400	0
Total sulfur, pct	1,900	400	91	.70	2.8	1,500	0	100
Organic sulfur, pct	1,900	400	100	.00	1.9	1,600	0	100
Pyritic sulfur, pct	1,650	230	50	.24	1.0	1,900	0	100
Sulfate sulfur, pct	1,900	300	25	.01	.06	1,500	400	0
Sulfur content per heating value, lb/MM Btu	1,900	400	91	.49	2.1	1,600	0	100
Volatile matter, pct	1,900	320	25	3.80	16	1,500	0	100
Heating value, Btu/lb	1,770	0	10	12,300	14,800	1,900	400	0

¹Entraining gas composition, hydrogen in nitrogen.

TABLE 2. — Data representing char yield and quality as a function of variable operating conditions ^{1/}

Run	X ₁ : Temperature, °F	X ₂ : Pressure, psig	X ₃ : Hydrogen, percent	Sulfur content ^{2/}			Sulfur per heating value, lb/MM	Volatile matter, pct of char	Heating value, Btu/lb	Char yield, lb/ton coal
				Total	Organic	Pyritic				
1	1,600	100	25	2.00	1.72	.23	.05	9.9	12,810	1,010
2	1,600	100	75	1.98	1.67	.27	.04	9.9	12,790	922
3	1,600	300	25	1.79	1.47	.27	.05	8.3	12,800	1,062
4	1,600	300	75	1.72	1.44	.24	.04	9.4	12,850	1,012
5	1,800	100	25	1.79	1.29	.48	.02	5.7	12,350	916
6	1,800	100	75	1.88	1.33	.51	.04	8.0	12,690	934
7	1,800	300	25	1.56	1.01	.54	.01	4.8	13,380	908
8	1,800	300	75	1.16	.66	.49	.01	5.5	12,530	854
15	1,900	200	50	1.29	.80	.46	.03	5.7	12,940	752
14	1,500	200	50	1.83	1.22	.56	.05	10.6	12,770	858
17	1,700	400	50	1.43	1.00	.38	.05	7.3	13,100	914
16	1,700	0	50	2.28	1.60	.64	.04	10.4	12,590	890
19	1,700	200	100	1.69	1.23	.41	.05	10.8	13,100	936
18	1,700	200	0	2.16	1.73	.39	.04	7.7	12,700	1,036
9	1,700	200	50	1.53	1.20	.31	.02	7.1	12,660	856
10	1,700	200	50	1.64	1.19	.43	.02	8.3	12,730	920
11	1,700	200	50	1.58	1.13	.40	.05	7.8	12,600	866
12	1,700	200	50	1.62	1.29	.27	.06	7.2	12,370	884
13	1,700	200	50	1.58	1.40	.16	.02	7.2	12,710	886

^{1/} Coal carbonized was Pittsburgh-bed high-volatile A bituminous with the following analysis: sulfur, 2.55 percent, volatile matter, 34.0 percent, and heating value, 14,090 Btu per pound.

^{2/} Concentration in char, weight-percent.

TABLE 4. — Comparison of Pittsburgh-bed high-volatile A bituminous coal and char produced at 1,900° F, 400 psig, and 91 pct H₂, 9 pct N₂ entraining gas

	Coal	¹ Char
Char yield, wt pct		34.0
Sulfur, wt pct		
Total	2.55	.70
Organic	1.49	.00
Pyritic	.93	.77
Sulfate	.13	.038
Sulfur-Btu ratio, lb/MM Btu	1.81	.49
Analysis, wt pct		
Volatile matter	33.98	7.38
Ash	7.28	15.68
Hydrogen	5.23	2.19
Total carbon	76.4	80.3
Fixed carbon	53.51	76.41
Water	.8	.8
Calorific value, Btu/lb	14,300	13,300

¹ All values are theoretical. Sum of the organic, pyritic, and sulfate sulfur percentages will not necessarily equal the value for total sulfur.

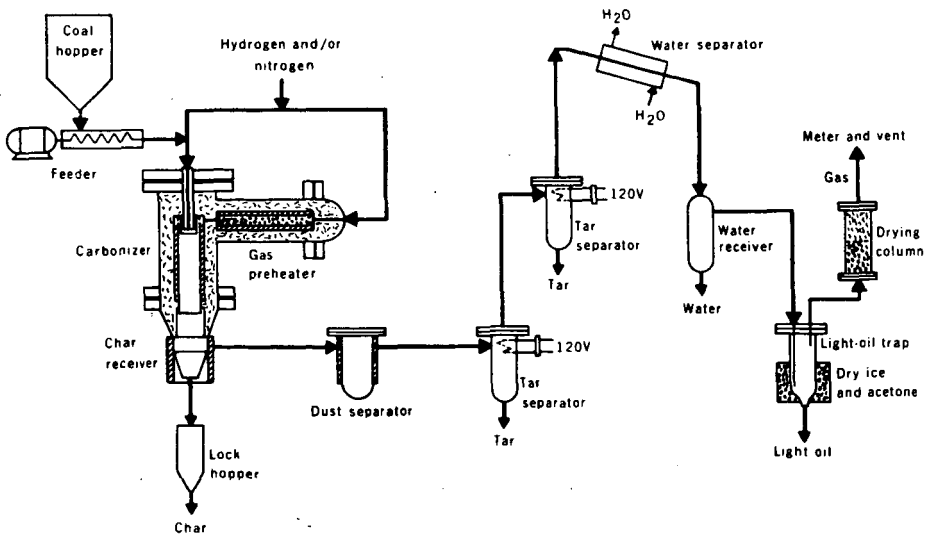
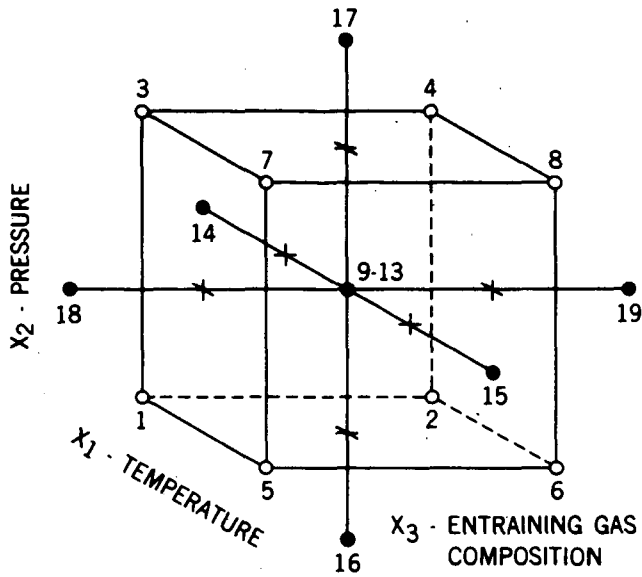


FIGURE 1. — Flow Diagram of Pressurized Coal Carbonization System



Location of Experimental Points

Experiment	Operating Variables		
	Temperature, °F	Pressure, psig	Entraining gas composition \mathcal{U}
1	1,600	100	25
2	1,600	100	75
3	1,600	300	25
4	1,600	300	75
5	1,800	100	25
6	1,800	100	75
7	1,800	300	25
8	1,800	300	75
9-13	1,700	200	50
14	1,500	200	50
15	1,900	200	50
16	1,700	0	50
17	1,700	400	50
18	1,700	200	0
19	1,700	200	100

\mathcal{U} Volume-percent H_2 in N_2

FIGURE 2. — Three-Factor Composite Design

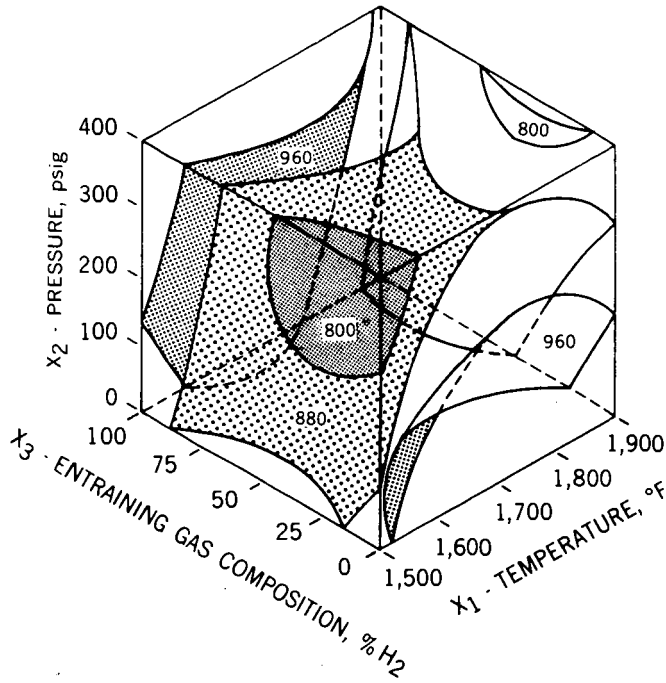


FIGURE 3. — Char Yield, lb/ton Coal

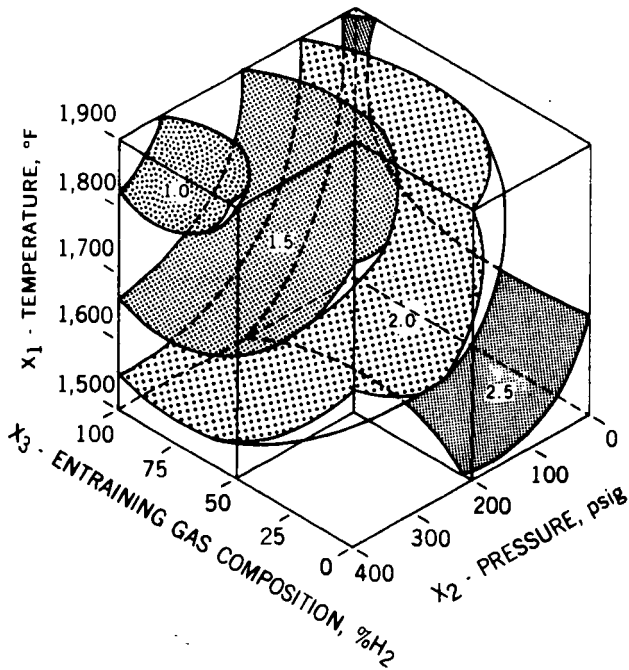


FIGURE 4. — Total Sulfur in Char, pct

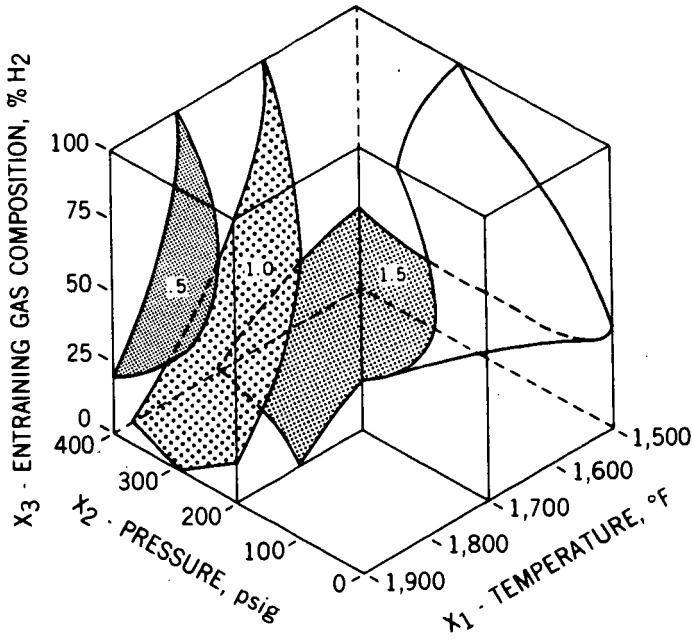


FIGURE 5. — Organic Sulfur in Char, pct

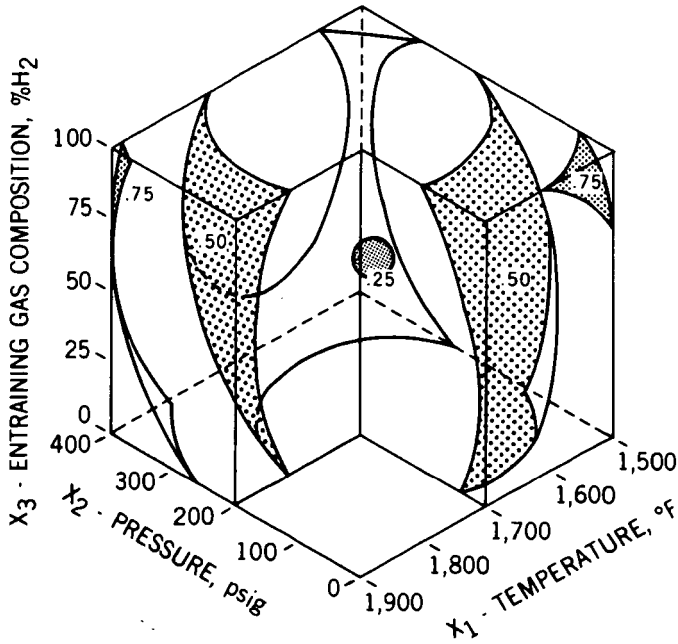


FIGURE 6. — Pyritic Sulfur in Char, pct

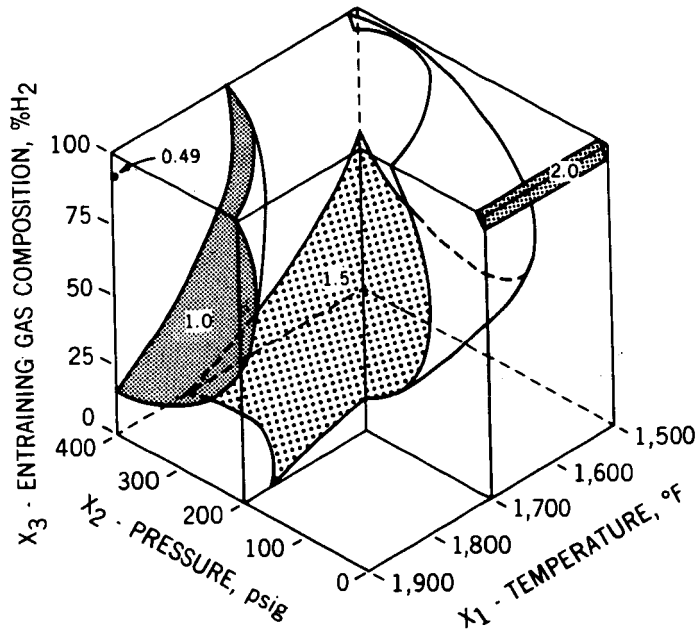


FIGURE 7. — Sulfur in Char per Unit Heating Value, lb S/10⁶ Btu

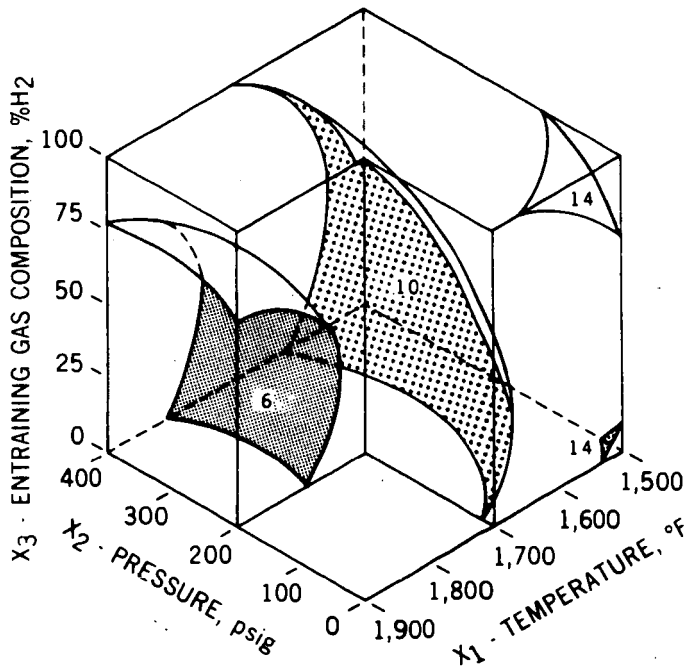


FIGURE 8. — Volatile Matter in Char, pct